

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21738 A1

- (51) International Patent Classification⁷: C10L 1/06
- (21) International Application Number: PCT/GB00/03569
- (22) International Filing Date:
15 September 2000 (15.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
9922553.4 23 September 1999 (23.09.1999) GB
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): BP OIL INTERNATIONAL LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).
- Published:
— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): BUTLER, Graham [GB/GB]; Ashby House, Star Hill, Churt, Surrey GU10 2HS (GB). CLARK, Alisdair, Quentin [GB/GB]; 18 Britten Close, Ash, Aldershot, Hampshire GU12 6LS (GB).
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
- (74) Agent: COLLINS, Frances, Mary; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).

(54) Title: FUEL COMPOSITIONS

(57) Abstract: Unleaded blend compositions, as well as formulated gasolines containing them have a Motor Octane Number (MON) of at least 80 comprising at least 10 % of component (a), which is at least one branched chain alkane of 8-12 carbons with at least 4 methyl or ethyl branches, and as component (b) at least 20 % of at least one, liquid hydrocarbon or mixture thereof of bp60-160 °C, especially of MON value at least 70 and RON at least 90 or as component (b) at least 20 % of one or more refinery streams. The component (a) gives rise to reduced emissions to the composition or gasoline on combustion.

WO 01/21738 A1

FUEL COMPOSITIONS

This invention relates to a fuel composition, in particular a gasoline composition for transportation uses e.g. use in motor vehicles or aircraft.

For many years manufacturers of spark ignition combustion engines have been striving for higher efficiency to make optimum use of hydrocarbon based fuels. But such engines require gasolines of higher octane number, which has been achieved in particular by addition of organo lead additives, and latterly with the advent of unleaded gasolines, by addition of MTBE. But combustion of any gasoline gives rise to emissions in the exhaust gases, e.g. of carbon dioxide, carbon monoxide, nitrogen oxides (NO_x) and toxic hydrocarbons and such emissions are undesirable.

Unleaded gasolines have been discovered having high Octane Number but producing low emissions on combustion.

The present invention provides an unleaded blend composition having a Motor Octane Number (MON) of at least 81 or 85 and Research Octane Number (RON) of at least 91 or 94 which comprises component (a) a total of at least 10% or 15% by volume of the blend composition of at least one branched chain hydrocarbon, which is an alkane of 8-12 carbon atoms with at least 4 methyl or ethyl branches (hereinafter called a compound (A) there being a minimum of at least 1, 2, 5 or 10% by volume (of the blend composition), of at least one individual compound (A) and component (b) at least one liquid hydrocarbon or mixture thereof of bp60-160°C having a MON value of at least 60 preferably at least 70 and RON value of at least 70 preferably at least 80 and especially at least 90, the total amount of component (b) being at least 20%, with the preferred proviso that the blend composition contains less than 5% of 223 trimethyl pentane, and

especially less than 1 or 0.5%, and especially less than 0.5%, in total of 223 trimethyl butane and 223 trimethyl pentane.

In another aspect the present invention provides an unleaded blend composition of MON value of at least 81 or 85 and RON value of at least 91 or 94 which comprises
5 component (a) as defined above and as component (b) at least 20% in total of one or more refinery streams, such that the blend composition contains in total at least 70% of saturated hydrocarbons.

Unless otherwise stated all percentages in this specification are by volume, and disclosures of a number of ranges of amounts in the composition or gasoline for 2 or
10 more ingredients includes disclosures of all sub-combinations of all the ranges with all the ingredients.

The compounds A are alkanes of 8-12 carbon atoms (especially 8 or 10 carbons) with at least 4 methyl and/or ethyl branches, e.g. 4-6 branches, preferably 4 or 5 or especially 4 branches. Methyl branches are preferred. The compounds usually have their
15 longest chain of carbon atoms, hereinafter called their backbone chain, with 4-7 e.g. 4-6 chain carbon atoms (especially 4 or 5) to which the methyl, and/or ethyl branches are attached. Advantageously, especially in relation to the first to tenth groupings as described further below, there are no branched groups constituting the branches other than methyl or ethyl, and, in the backbone chain of carbon atoms, there are especially no
20 linear alkyl groups of more than 2 carbons nor 1,2 ethylene or 1,3 propylene groups in the chain, and especially no methylene groups in the chain except as part of an ethyl group; thus there are especially no n-propyl or n-butyl groups forming part of the backbone chain. Preferably there is at least one compound (A) alkane of 9-12 e.g. 9 or 10 carbons, and in this case there is usually less than 50% or 10% of an 8 carbon alkane
25 compound e.g. with 3 methyl branches.

The compounds can have 1 or 2 methyl or ethyl groups attached to the same carbon atom of the backbone chain, especially 1 or 2 methyl groups and 0 or 1 ethyl groups. The carbon atom in the backbone at which the branching occurs is non-terminal i.e. is an internal carbon in the backbone chain, especially the 2, 3 and/or 4 numbered
30 carbon in the backbone. Thus advantageously the compound has geminal methyl substituents on position 2, 3 or 4 carbon atoms, especially position 2, but in particular position 3.

In a first grouping of compounds A, there is at least one pair of geminal methyl branch substituents, and they are on position 2, or there are 2 or 3 pairs of geminal branches at least 2 pairs being on vicinal (ie adjacent) carbon atoms, as in a group -CMe₂-CMe₂-.

- 5 In a second grouping of the compounds A there are 1, 2 or 3 pairs of geminal methyl branch substituents on a 4-6 carbon chain backbone, and, if any Ethyl CMe₂- structure is present, then there are 2 Ethyl CMe₂ groups in the compound. The compounds of the second grouping advantageously have a MON value of at least 100.

- 10 In a third grouping of the compounds, there is one geminal methyl branch grouping i.e. -CMe₂- on the backbone, while on one or both of the adjacent carbon atoms of the backbone, there is/are one or two methyl or ethyl branches/especially 1 or 2 methyl branches.

- 15 In a fourth grouping of the compounds there are one, two or three pairs of geminal methyl branches. If there are 2 or 3 pairs then at least 2 pairs are on adjacent backbone carbon atoms, and if there is only one pair, then they are preferably on the 2 position backbone carbon and there is a methyl branch at least on the 3 position backbone carbon. Such compounds usually have a RON value of at least 111. Advantageously the compounds are of 8 or 10 carbon atoms.

- 20 In a fifth grouping the compound A has 2 or 3 pairs of geminal methyl branches at least 2 pairs being on adjacent backbone carbon atoms, and the compound has a symmetrical structure. Such compounds usually have RON value of at least 120, and especially are of 8 or 10 carbon atoms.

- 25 In a sixth grouping the compounds have a linear backbone chain of 4 or 6 carbons and have 4-6 e.g. 4, 5 or 6 especially 4 methyl branches, in at least one geminal group (CMe₂) especially in the absence of a 1,2 ethyl group in the backbone.

- 30 In a seventh grouping, the compounds have a linear backbone chain of 5 or 6 carbons and have 4-6 e.g. 4, 5 or 6 especially 4 branches in at least one geminal group, with the proviso that if there are 4 methyl branches and the compound contains an Ethyl CMe₂ group, then the compound contains two such Ethyl CMe₂ groups. Such compounds are usually liquid at 25°C and generally have a RON value of greater than 105. Especially there are only methyl branches; such compounds usually have a MON value of at least 101.

Advantageously in an eighth grouping the compounds A contain 1, 2 or 3 carbon atoms with geminal methyl branches, and if there is only one such carbon atom with geminal branches, then there is/are one or two branches on a vicinal carbon atom to the geminal one, and any ethyl -C- chain group in the backbone chain has 5 carbon atoms i.e. is (Ethyl)₂CH or Ethyl CMe₂-. Especially there are 2 or 3 vicinal carbon atoms in the backbone, each carrying 2 methyl branches.

A particularly preferred sub-class (ninth grouping) for the compound A is alkanes with alkyl substituents on vicinal internal carbon atoms, with a total of 4, 5 or 6 carbon atoms in said substituents.

Among this sub-class are preferred ones especially with geminal methyl groups on internal chain carbon atoms. Particularly preferred sub-class compounds A have 4 or 5 methyl substituents on the carbon backbone, especially with at least 2 on the same backbone carbon atom (in particular in two -CMe₂- groups) especially in a -CMe₂-CMe₂ group.

In another aspect of the invention there is provided an unleaded blend composition having a MON value of at least 81 or 85 and RON value of at least 91 or 94, which comprises component (a) a total of at least 10 or 15% of one or more branched alkane compounds A¹ of 8-12 carbons (especially with 4-7 or 4-6 backbone carbon atoms), with at least 4 methyl or ethyl branches and with at least 2 backbone carbon atoms which are secondary and/or tertiary carbon atoms, with the proviso that if there are only 2 such carbon atoms, then both are tertiary, there being a minimum of at least 1, 2, 5 or 10% (by volume of the composition) of at least one individual compound A¹, and component (b) of nature and in amount as described herein, with the preferred proviso as described above. In the above component A¹, which may be the same or different from A, there may thus in a tenth grouping be in the backbone internal (i.e. non-terminal) carbon atoms which are (i) 2 or 3 tertiary carbons, (ii) especially vicinal ones, or (iii) 2 tertiary and one sec. carbon or (iv) 2 tertiary and one or 2 primary carbon, or (iv) 1 or 2 tertiary and 1 or 2 sec subject to at least 4 branches, in particular (vi) with the tert and a sec. carbon vicinal and (vii) when there are 2 tert, these are vicinal or non-vicinal and (viii) with 1 or 2 vicinal tert and sec. carbons subject to at least 4 branches. The compounds A¹ usually are free from 2 primary internal backbone carbon atoms on vicinal carbons i.e. as in 1,2-ethylene group. Preferably any primary internal backbone carbon atoms are not between,

e.g. adjacent on both sides to, a tert and/or sec, carbon on the one hand and a tert and/or sec. carbon on the other hand. Especially at least the said 2 backbone carbon atoms above in compounds A^1 are vicinal.

In another category, the eleventh grouping is of compounds A^1 which contain,
5 with the proviso of at least 4 branched groups, (i) as at least one end of the backbone a group of formula CHR^1R^2 where each of R^1 and R^2 , which are the same or different is a methyl or ethyl group or (ii) as at least one end of the backbone a group of formula $CR^1R^2R^3$ where R^1 and R^2 are as defined above and R^3 is methyl or ethyl. Preferred are such compounds A^1 which have both (i) and (ii), especially when the CHR^1R^2 group is
10 $CHMe_2$ when the compound has 8 carbons or a backbone of 5 carbons and when all internal carbon atoms in the backbone chain are secondary or tertiary.

The compounds A or A^1 may have a boiling point at 1 bar pressure of 150-175°C, 130-140°C, 110-129°C, or 90-109°C. In particular the boiling point is preferably at least 105°C e.g. 105-175°C, with the preferred proviso that it is at least 112°C such as 112-
15 175°C unless the compound A or A^1 has 4 alkyl branches.

In another category the compounds A or A^1 may have 4-6 methyl and/or ethyl branches on a 4-7 or 4-6 carbon backbone, and especially a ratio of carbon atom in branches to carbon atoms in the backbone chain of at least 0.63:1 e.g. 0.63-1.6:1 such as 0.63-1.0:1. The compounds usually have 9 or 10 carbons, unless the above ratio is at
20 least 0.63, 0.75 or 0.9.

Preferred compounds are 3344 tetramethyl hexane (A1), 2233 tetramethyl butane (A2), 2233 tetramethyl pentane (A7), 22334 pentamethyl pentane (A12) 22344 pentamethyl pentane (A13) 2334 tetramethyl pentane (A14) 2234 tetramethyl pentane (A15) 223344 hexamethyl pentane (A16) 22446 pentamethyl heptane. Of these (A1) and (A2) are most preferred with (A7) being also very valuable.
25

The compounds A and A^1 are either known compounds and may be made according to the published literature, or are novel and may be made by conventional methods known per se in the literature (e.g. as described in Kirk Othmer Encyclopaedia of Chemical Technology 3rd Ed. Publ. Wiley). Examples of suitable methods of
30 preparation are known carbon-carbon coupling techniques for making alkanes. The technique may involve reactions of one or more usually 1 or 2 alkyl chlorides, bromides or iodides with an elemental metal of Group IA, IIA, IB or IIB of the Periodic Table in

Advanced Inorganic Chemistry by F.A.Cotton + G.wilkinson, Pub. Interscience New York 2nd Ed. 1966, especially sodium, magnesium, or zinc. The alkyl halide is usually a branched chain one of 3-6 carbons, in particular with methyl or ethyl branches, and especially with the halogen atom attached to a CMe_2 group in at least one of the alkyl

5 halides. Preferably the halide is of formula MeCMe_2X or EtCMe_2X , where X is Cl, Br or I, and the other halide, if any, is a tertiary alkyl halide or a secondary one e.g. of formula RR^1CHX , wherein at least one of R and R^1 is a branched alkyl group e.g. of 3-5 carbons such as isopropyl or t-butyl, and the other (if any) is methyl or ethyl or a primary

10 branched alkyl halide e.g. of formula $\text{R}^{11}\text{CH}_2\text{X}$, where R^{11} is a branched alkyl group 4-5 carbons with methyl or ethyl branches, such as isobutyl or isoamyl. Alternatively both halides can be secondary e.g. of formula RR^1CHX , as defined above and $\text{R}^{11}\text{R}^{\text{IV}}\text{CHX}$ where R^{11} is methyl or ethyl and R^{IV} is as defined for R, such as isopropyl or one can be secondary (as above) and one can be primary e.g. methyl or ethyl halide. The methods of coupling optimum for any particular compound A or A^1 depend on availability of the

15 precursor alkyl halide(s) so that in addition to the above kinds, coupling via methyl or ethyl halides with branched alkyl halides of 6-9 carbons may also be used e.g. pentamethyl ethyl bromide and methyl magnesium bromide to form A2. The alkyl halide(s) can react together in the presence of the metal (as in a Wurtz reaction with sodium), or one can react first with the metal to form an organometallic compound e.g. a

20 Grignard reagent or organo zinc, followed by reaction of the organometallic with the other alkyl halide. If desired the Grignard reagent reaction can be in the presence of a metal of Group IB or IIB, such as silver, zinc or copper (especially high activity copper). If desired the Grignard reagent from one or both alkyl halides can be reacted with the latter metal to form other alkyl metallic species e.g. alkyl silver or alkyl copper

25 compounds, which can disproportionate to the coupled alkane. The Grignard reagent(s) can also react with a cuprous halide to form alkyl copper species for disproportionation. Finally an organometallic compound, wherein the metal is of Group IA or IIA e.g. Li or Mg can be coupled by reaction with a cuprous complex to give a coupled alkane. Use of only 1 alkyl halide gives a symmetrical alkane, while use of a mixture of alkyl halides

30 gives a mixture of alkanes, usually each of the symmetrical dimers and an unsymmetrical alkane formed from both alkyl halides.

The above organometallic reactions are usually conducted under inert conditions,

i.e. anhydrous and in the absence of oxygen e.g. under dry nitrogen. They are usually performed in an inert solvent e.g. a dry hydrocarbon or ether. At the end of the reaction any residual organometallic material is decomposed by addition of a compound with active hydrogen e.g. water or an alcohol, and the alkanes are distilled off, either directly
5 or after distribution between an organic and aqueous phase.

Examples of the above processes are the coupling of tertbutyl chloride in the presence of Mg and diethyl ether to form compound A(2) (as described by D.T.Flood et al, J.Amer Chem. Soc. 56, (1934) 1211, or R.E.Marker et al, J.Amer Chem. Soc. 60, (1938) 2598 or F.C.Whiteman et al, J.Amer Chem. Soc. 55, (1933) 380), and the
10 corresponding coupling of EtCMe₂ halides to form compound A1. Other preparations of highly branched alkanes are described in M Tamura and J.Kochi, J.Amer. Chem. Soc. Vol.93, Part 6 (March 24, 1971) and F.O.Ginah et al, J. Org. Chem. Vol. 199, 55 pp584-589 and R.Y.Levina & V.K.Daukshas, Zhur.Obschei Khim. Vol. 29 (1959) and F L Howard et al, J Res. Nat. Bur. Standards Research Paper RP1779, Vol 38 March
15 1947 pp 365-395. The disclosures of these documents is incorporated herein by reference.

The crude alkanes made by the above processes, especially the symmetrical ones, may be used as such in the blends of the invention or may be purified further e.g. by distillation first. The crude unsymmetrical alkanes may be also purified, but are
20 preferably used as such as the by-product alkanes are often useful hydrocarbons for the blend, e.g. coupling of t BuX and EtCMe₂X as described above produces a mixture of alkanes containing A1, A2 and A7.

Other known methods of making the alkanes A or A¹, are reaction of alkyl metallic compounds e.g. Grignard reagents with carbonyl compounds such as aldehydes, ketones,
25 esters, or anhydrides to form branched chain carbinols, which are dehydrated to the corresponding olefin, which is hydrogenated to the alkane. Thus 2,2,3,4-tetra methyl pentane may be made from isopropyl magnesium bromide and methyl t-butyl ketone (followed by dehydration and hydrogenation),

Thus the present invention produces an unleaded blend composition of MON value
30 at least 81 or 85 and RON value at least 91 or 94 which comprises (a) a total of at least 10 or 15% of one or more branched hydrocarbon compound A or A¹ there being a minimum of at least 1, 2 or 5% of at least one individual compound A or A¹ and (b) at

least 20% of at least one different liquid hydrocarbon of bp60-160°C having a MON value of at least 70 and RON value at least 90 especially when (b) is not within the definition of A or A¹. Examples of the liquid hydrocarbons are paraffins, such as linear or branched chain alkanes of 4-8 carbons, such as isobutane, butane, isopentane,
 5 dimethyl alkanes such as 2,3 dimethyl butane, cycloalkanes, such as cyclopentane and cyclohexane, aromatics and olefins.

Another unleaded blend composition of the invention of MON value of at least 81 or 85 and RON value of at least 91 or 94 comprises component (a) as above and component (b) at least 20% of at least one of a straight run naphtha, alkylate isomerate
 10 (bp25-80°C) heavy reformat, light reformat (bp20-79°C), hydrocrackate, aviation alkylate (bp30-190°C), straight run gasoline, cracked spirit, such as heavy or light catalytic cracked spirit or steam cracked spirit. The straight run products are produced directly from crude oil by atmospheric distillation. The naphtha may be light naphtha of bp30-90°C or medium naphtha of bp90-150°C or heavy naphtha of bp150-220°C.

15 In the blends of the invention, the amount of at least one individual compounds A or A¹ is usually at least 1, 2 or 5%, or at least 10 or 15%, such as 5-60%, e.g. 15-60%, or 8-25%, 20-35% or 30-55% or 2-10%. The amount of 2,2,4-trimethyl pentane if present is usually at least 10% of the composition. Total amounts of trimethyl pentanes in the blend are preferable less than 69% of the blend, but advantageously at least 26%
 20 (especially when the amount of aromatics is less than 17%). If a 9 or 10 carbon alkane is (a), then the amount of 2,2,4-trimethyl pentane is especially less than 70 or 50%. More than one such compound A or A¹ may be present e.g. of higher and lower RON in weight ratios of 9:1 to 0.5:99.5, such as 0.5:1 to 5:1 or 5:95 to 20:80, particularly for mixtures of compounds A1 and A2 and/or with higher or lower boiling points
 25 (atmospheric pressure) e.g. those in which the compounds A and/or A¹ have boiling points differing by at least 10°C e.g. at least 40°C such as 10-70°C or 20-50°C the relative amounts being as described above. In the blends amounts of compounds A or A¹ of RON at least 138 e.g. A1 may be 1-40%, such as 2-10 or 20-35%, while those of compounds A or A¹ of RON 120-138 e.g. A2 may be 1-60, such as 5-60, 8-25 or 30-
 30 55% (especially when used with the higher RON compound) or 15-50% when used as sole compound A. Total amounts of all compounds A and A¹ (if any) in the blend are at least 10 or 15% such as 15-70 e.g. 15-60, 15-40 or 30-55% or 40-60% or 10-35%.

The blend may also comprise predominantly aliphatic refinery streams which are usually liquid e.g. at 20°C such as naphtha, straight run gasoline (also known as light naphtha bp 25-120°C), alkylate and isomerate. Amounts in total of these may be 10-70%, such as 10-30, 30-70 or 35-65%. Amounts of naphtha may be 0-70% or 1-70%
5 such as 10-30, 30-70 or 35-65%, while amounts of light naphtha may be 0 or 1-70 such as 1-20 or especially 30-65%, and amounts of medium naphtha may be 0 or 1-55, such as 3-20 or 15-55%. The volume ratio of light to medium naphtha may be 50:1 to 1:50, such as 0.5-20:1 or 1:0.5-50. Amounts of alkylate or isomerate (if present) may be 0.5-20% such as 1-10%, while amounts of hydrocrackate may be 0.5-30% e.g. 10-30%. A
10 preferred blend comprises 20-60% compound A or A¹ and conversely 80-40% straight run gasoline, the sum of these being substantially 100%.

The blends of the invention usually contain in total at least 70% of saturates, such as 70-98% or 70-90% or 90-98%.

If desired and especially for aviation gasoline, the blends may contain a
15 hydrocarbon component which is a saturated aliphatic hydrocarbon of 4-6 carbons and which has a boiling point of less than 80°C under atmospheric pressure, such as 20-50°C, and especially is itself of Motor Octane Number greater than 88 in particular at least 90 e.g. 88-93 or 90-92. Examples of the hydrocarbon component include alkanes of 4 or 5 carbons in particular iso-pentane, which may be substantially pure or crude hydrocarbon
20 fraction from reformat or isomerate containing at least 30% e.g. 30-80% such as 50-70%, the main contaminant being up to 40% mono methyl pentanes and up to 50% dimethyl butanes. The hydrocarbon component may be an alkane of boiling point (at atmospheric pressure) -20°C to +20°C e.g. n and/or iso butane optionally in blends with the C₅ alkane of 99.5:0.5 to 0.5:99.5, e.g. 88:12 to 75:25. n Butane alone or mixed with
25 isopentane is preferred, especially in the above proportions, and in particular with a volume amount of butane in the composition of up to 20% such as 1-15% e.g. 1-8, 3-8 or 8-15%, especially 1-3.5%.

The hydrocarbon component boiling less than 80°C, in particular isopentane, may also be present in compositions of the invention which contain at least one compound A
30 or A¹, of at least 10 carbon atoms, in particular those boiling at 160°C or above, such as A1, and A12-14. Relative amounts of these compounds A or A¹ to the low boiling component e.g. isopentane, may be 1-9:9-1 such as 5-9:5-1, especially with less than

20% of A or A¹ in the composition.

Cycloaliphatic hydrocarbons e.g. of 5-7 carbons such as cyclopentane or cyclohexane may be present but usually in amounts of less than 15% of the total e.g. 1-10%.

- 5 The compositions of the invention also preferably contain as component (d) at least one olefin, (in particular with one double bond per molecule) which is a liquid alkene of 5-10 e.g. 6-8 carbons, such as a linear or branched alkene e.g. pentene, isopentene hexene, isohexene or heptene or 2 methyl 2 pentene, or a mixture comprising alkenes which may be made by cracking e.g. catalytically or thermally cracking a residue from
- 10 crude oil, e.g. atmospheric or vacuum residue; the mixture may be heavy or light catalytically cracked spirit (or a mixture thereof). The cracking may be steam assisted. Other examples of olefin containing mixtures are "C6 bisomer", catalytic polymerate, and dimate. The olefinic mixtures usually contain at least 10% w/w olefins, such as at least 40% such as 40-80% w/w. Preferred mixtures are (xi) steam cracked spirit (xii)
- 15 catalytically cracked spirit (xiii) C6 bisomer and (xiv) catalytic polymerate, though the optionally cracked catalytically spirits are most advantageous. Amounts in the total composition of the olefinic mixtures especially the sum of (xi) - (xiv) (if any present) maybe 0-55, e.g. 10-55 or 18-37 such as 23-35 or 20-55 such as 40-55% Amounts of (xi) and (xii) (if present) in total in the composition are preferably 18-55, such as 18-35,
- 20 18-30 or 35-55% (by volume).

The olefin or mixture of olefins usually has an MON value of 70-90, usually a RON value of 85-95 and a ROAD value of 80-92.

- The volume amount of olefin(s) in total in the gasoline composition of the invention may be 0% or 0-30%, e.g. 0.1-30% such as 1-30% in particular 2-25 e.g. 2-
- 25 14% (especially 3-10). Usually the composition contains at least 1% olefin and a maximum of 18% or especially a maximum of 14%, but may be substantially free of olefin.

- The compositions may also contain as component (e) at least one aromatic compound, preferably an alkyl aromatic compound such as toluene or o, m, or p xylene
- 30 or a mixture thereof or a trimethyl benzene. The aromatics may have been added as single compounds e.g. toluene, or may be added as an aromatics mixture containing at least 30% w/w aromatic compounds such as 30-100% especially 50-90%. Such

mixtures may be made from catalytically reformed or cracked gasoline obtained from heavy naphtha. Example of such mixtures are (xxi) catalytic reformat and (xxii) heavy reformat or heavy steam cracked spirit. Amounts of the single compounds e.g. toluene in the composition may be 0-35%, such as 2-33% e.g. 10-33%, while amounts of the aromatics mixtures especially the total of the reformates (xxi) & (xxii) (if any) in the composition may be 0-50%, such as 1-33% e.g. 2-15% or 2-10% or 15-32% v/v, and total amount of reformates (xxi), (xxii) and added single compounds (e.g. toluene) may be 0-50% e.g. 0.5-20% or 5-40, such as 15-35 or 5-25% v/v.

The aromatics usually have a MON value of 90-110 e.g. 100-110 and a RON value of 100-120 such as 110-120 and a ROAD value of 95-110. The volume amount of aromatic compounds in the composition is usually 0% or 0-50% such as less than 40% or less than 28% or less than 20% such as 1-50%, 2-40%, 3-28%, 4-25%, 5-20% (especially 10-20%), 4-10% or 20-35% especially of toluene. The gasoline composition may also be substantially free of aromatic compound. Amounts of aromatic compounds of less than 42%, e.g. less than 35% or especially less than 30% or 18% are preferred. Preferably the amount of benzene is less than 5% preferably less than 1.5% or 1% e.g. 0.1-1% of the total volume or less than 0.1% of the total weight of the composition.

The compositions may also contain as component (f) at least one oxygenate octane booster, usually of Motor Octane Number of at least 96-105 e.g. 98-103. The oxygenate may be any organic liquid molecule containing and preferably consisting of, CH and at least one oxygen atom e.g. 1-5 of bp less than 225°C. The octane booster is usually an ether e.g. a dialkyl ether, in particular an asymmetric one, preferably wherein each alkyl has 1-6 carbons, in particular one alkyl being a branched chain alkyl of 3-6 carbons in particular a tertiary alkyl especially of 4-6 carbons such as tert-butyl or tert-amyl, and with the other alkyl being of 1-6 e.g. 1-3 carbons, especially linear, such as methyl or ethyl. Examples of such oxygenates include methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether and methyl tertiary amyl ether. The oxygenate may also be a cyclic ether, in particular with 5 or 6 ring atoms in the or each ring, such as furan or tetrahydrofuran and its lower alkyl e.g. methyl derivatives. The oxygenate may also be an alcohol of 1-6 carbons e.g. ethanol. The oxygenate may also be an organic carbonate e.g. a dialkyl carbonate with 1-3 carbon atoms in each alkyl e.g. dimethyl carbonate.

The volume amount of the oxygenate may be 0 or 0-25% such as 1-25%, 2-20%,

2-10% or 5-20% especially 5-15%, but advantageously less than 3% such as 1-3% (especially of MTBE and/or ethanol). The oxygenate may also be substantially absent from the composition or gasoline of the invention, which is thus a substantially hydrocarbon fuel.

5 The present invention also provides a formulated unleaded gasoline comprising a blend composition of the invention comprising component (a) and (b) and usually at least one gasoline additive, e.g. as described above, in particular with the gasoline comprising less than 5%, e.g. less than 4% of triptane or 223 trimethyl pentane.

10 The blend of the invention contains at least one component (a) and component (b) and, (optionally (c) to (f), as well, and the formulated unleaded gasoline also contains at least one gasoline additive e.g. a motor gasoline or aviation gasoline additive, for example as listed in ASTM D-4814 the contents of which is herein incorporated by reference or specified by a regulatory body, e.g. US California Air Resources Board (CARB) or Environmental Protection Agency (EPA). These additives are distinct from
15 the liquid fuel ingredients, such as MTBE. Such additives may be the lead free ones described in Gasoline and Diesel Fuel Additives, K Owen, Publ. By J.Wiley, Chichester, UK, 1989, Chapters 1 and 2, USP 3955938, EP 0233250 or EP 288296, the contents of which are herein incorporated by reference. The additives maybe pre-combustion or combustion additives. Examples of additives are anti-oxidants, such as one of the amino
20 or phenolic type, corrosion inhibitors, anti-icing additives e.g. glycol ethers or alcohols, engine detergent additives such as ones of the succinic acid imide, polyalkylene amine or polyether amine type and anti-static additives such as ampholytic surface active agents, metal deactivators, such as one of thioamide type, surface ignition inhibitors such as organic phosphorus compounds, combustion improvers such as alkali metal salts and
25 alkaline earth metal salts of organic acids or sulphuric acid monoesters of higher alcohols, anti valve seat recession additives such as alkali metal compounds, e.g. sodium or potassium salts such as borates or carboxylates e.g. sulpho succinates, and colouring agents, such as azodyes. One or more additives (e.g. 2-4) of the same or different types may be used, especially combinations of at least one antioxidant and at least one
30 detergent additive. Antioxidants such as one or more hindered phenols e.g. ones with a tertiary butyl group in one or both ortho positions to the phenolic hydroxyl group are preferred in particular as described in Ex.1 hereafter. In particular the additives may be

present in the composition in amounts of 0.1-100ppm e.g. 1-20ppm of each, usually of an antioxidant especially one or more hindered phenols. Total amounts of additive are usually not more than 1000ppm e.g. 1-1000ppm.

5 The compositions and gasolines are free of organolead compounds, and usually of manganese additives such as manganese carbonyls.

The compositions and gasolines may contain up to 0.1% sulphur, e.g. 0.000-0.02% such as 0.002-0.01%w/w.

10 The gasoline compositions of the invention usually have a MON value of 80 to 105 such as 85-105, 85-90, 90-105 or 93-105 e.g. but especially 94-102. The RON value is usually 90-115 e.g. 102-115 such as 98-112 or 105-112, or 93-98 e.g. 94.5-97.5, or 97-101 while the ROAD value is usually 85-110 or 85-107 e.g. 98-106 or 102-108 or 85-95. Preferred gasoline compositions have MON 83-93, RON 93-98 and ROAD 85-95 or MON 85-90, RON 94-101 and ROAD 89-96 but especially MON 93-98, RON 102-108, ROAD 98-106, or MON 95-105, RON 102-115 e.g. 108-115 and ROAD 98-106.

15 The Net calorific value of the gasoline (also called the Specific Energy) is usually at least 18000 Btu/lb e.g. at least 18500, 18700 or 18,900 such as 18500-19500, such as 18700-19300 or 18900-19200; the calorific value may be at least 42MJ/kg e.g. at least 43.5 MJ/kg such as 42-45 or 43-45 such as 43.5-44.5MJ/kg. The gasoline usually has a boiling range (ASTM D86) of 20-225°C, in particular with at most 5% e.g. 0-5% or 1-3% boiling in the range 161-200°C. The gasoline is usually such that at 70°C at least 10% is evaporated while 50% is evaporated on reaching a temperature in the range 77-120°C preferably 77-116°C and by 185°C, a minimum of 90% is evaporated. The gasoline is also usually such that 8-50% e.g. 10-40% may be evaporated at 70°C, 40-74% at 100°C, 70-99.5% at 150°C and 90-100% may be evaporated at 180°C; preferably 25 46-65% has been evaporated by 100°C. The Reid Vapour Pressure of the gasoline at 37.8°C measured according to ASTM D323 is usually 30-120, e.g. 40-100 such as 61-80 or preferably 50-80, 40-65, e.g. 45-65, 40-60 or 40-50Kpa. Especially the gasoline or blend has RON value of 90-115, MON value of 85-105, aromatics content of less than 35%, olefins content of less than 14%, benzene less than 1%, % evaporated at 70°C 10-40%, % evaporated at 100°C 40-74%, % evaporated at 150°C 70-99.5% and RVP of 30 40-60 kPa.

The gasoline compositions, when free of any oxygenates usually have a H:C atom

ratio of at least 1.8:1 e.g. at least 2.0:1 or at least 2.1 or 2.2:1, such as 1.8-2.3:1 or 2.0-2.2:1. Advantageously the gasoline composition meets the following criteria.

Atom H:C x [1 + oxy] x [Net Heat of Combustion + ROAD] ≥ y,

200

- 5 wherein Atom H:C is the fraction of hydrogen to carbon in the hydrocarbons in the composition, oxy means the molar fraction of oxygenate, if any in the composition, Net Heat of Combustion is the energy derived from burning 1lb (454g) weight of fuel (in gaseous form) in oxygen to give gaseous water and carbon dioxide expressed in Btu/lb units [MJ/kg times 430.35], and y is at least 350, 380, 410 or 430, in particular 350-440
10 e.g. 380-420 especially 400-420.

- Among preferred blends of the invention are unleaded blends comprising as component (a) at least 5 or 10% of at least one individual compound A or A¹ and component (b) as defined above, with the proviso that when the compound A or A¹ is an alkane of 9 or 10 carbon atoms, then blend contains at least 10% of an alkane of 6 or 7
15 carbons of MON at least 70 and RON at least 90, and preferably contains less than 5% in total of 2,2,3-trimethyl pentane and 2,2,3-trimethyl butane.

- Preferred formulated unleaded gasolines of the invention comprise at least one gasoline additive and the preferred unleaded blend above, with the proviso when the compound A or A¹ is an alkane of 9 or 10 carbon atoms, the blend preferably contains
20 less than 5% in total of 2,2,3-trimethyl pentane and 2,2,3-trimethyl butane.

- Preferred blends and gasolines of the invention can have MON values of 94-105 (e.g. 97-105), RON values of 103-115 (e.g. 107-115), ROAD values of 98-110 (e.g. 102-110), compound A or A¹ contents of 30-60% e.g. 40-60% (comprising 1 or 2 compounds A or A¹ especially A1 and/or A2), total naphtha contents of 35-65% (e.g.
25 35-55%) and 1-5% butane, the blends containing 1-8% e.g. 2-6% aromatics, 0-1% olefins and 91-99% (e.g. 94-98%) saturates. These are substantially aliphatic blends and gasolines of very high octane numbers, without the use of oxygenates such as MTBE, and also substantially saturated.

- Other very high octane blends and gasolines of the invention can have MON values
30 of 94-102 e.g. 94-99, RON values of 105-115, ROAD values of 99-107, compound A or A¹ contents of 30-60% e.g. 30-50% (comprising 1 or 2 compounds A or A¹ especially A1 and/or A2), medium naphtha contents of 5-30% and contents of total olefinic fraction

such as steam cracked spirit of 30-50% and 1-5% butane, the blends containing 10-25% aromatics e.g. 12-18% aromatics, 4-14% olefins e.g. 6-12%, and 60-90% such as 70-80% saturates. These high octane materials are obtained without the use of oxygenates.

Further blends and gasolines of the invention can have MON values of 84-90,
5 RON values of 93-98, ROAD values of 86-94, and contain compound A or A¹ in amount of 15-35% (especially of A2), total naphtha of 40-65% and olefinic fractions such as steam cracked spirit of 15-45% and 0 or 1-5% butane, with aromatic contents of 5-25% such as 10-18% olefin contents of 2-14% and saturate contents of 70-90%.

Other blends and gasolines of the invention can contain 10-35% compound A or
10 A¹ (especially A2), and naphtha 30-50%, hydrocrackate 10-30% alkylate and/or isomerate 2-10%, and reformat 3-12%.

Other blends and gasolines of the invention can contain 10-35% compound A or
A¹ (especially A2) and 3-12% reformat, 1-20% light naphtha/straight run gasoline, as well as alkylate and isomerate, the blend and gasoline preferably containing at least 70%
15 of saturates.

The invention can provide motor gasolines, in particular of 91, 95, 97, 98 and 110 RON values, with desired high Octane Levels but low emission values on combustion in particular of at least one of total hydrocarbons, NO_x, carbon monoxide, and carbon dioxide, especially of both total hydrocarbons and carbon dioxide. Thus the invention
20 also provides the use of a compound A particularly A1 or A2 in unleaded gasoline of MON at least 80 e.g. 80 to less than 98, e.g. as an additive to or component therein, to reduce the emission levels on combustion, especially of at least one of total hydrocarbons, NO_x, carbon monoxide and carbon dioxide especially both of total hydrocarbons and carbon dioxide. The invention also provides a method of reducing
25 emissions of exhaust gases in the combustion of unleaded gasoline fuels of MON of at least 80 which comprises having at least 10% component (a), in particular A1 or A2, present in the fuel which is a gasoline of the invention. The invention also provides use of an unleaded gasoline of the invention in a spark ignition combustion engine to reduce emissions of exhaust gases. In the compositions, gasolines, methods and uses of the
30 invention the component (a) is preferably used in an emission-reducing effective amount. The compositions of the invention may be used in supercharged or turbocharged engines, or in normally aspirated ones. The compound A, preferably A1 or A2, can

reduce one or more of the above emission levels better than a mixture of aromatics and oxygenate at similar Octane Number and usually decrease the fuel consumption as well.

The gasolines of the invention may be used in internal combustion spark ignition engines. They may be used to power moving vehicles on land and/or sea and/or in the air; the invention also provides a method of moving such vehicles by combustion of a gasoline of the invention. The vehicle usually has a driver and especially means to carry at least one passenger and/or freight.

The engine sizes for motor gasoline use are usually at least 45cc e.g. 45-10000cc e.g. at least 200cc, such as 500-10000cc, in particular 950-2550, such as 950-1550, or 1250-1850cc, or 2500-10000cc such as 2500-5000 or 5000-9000cc. The engines have at least 1 cylinder, but preferably at least 2 or 3 cylinders, e.g. 3-16, especially 4-6 or 8 cylinders; each cylinder is usually of 45-1250cc e.g. 200-1200cc, in particular 240-520cc or 500-1000cc. The engines may be 2 stroke engines, but are preferably 4 stroke. Rotary engines e.g. of the Wankel type may be used. The motor engines may be used to power vehicles with at least 2 wheels e.g. 2-4 powered wheels, such as motor bicycles, tricycles, and 3 wheeled cars, vans and motor cars, in particular those vehicles legislated for use on a public highway but also off road e.g. 4 wheeled drive vehicles, sports cars for highway use, and racing cars, including drag racing cars and track racing cars. Power from the engine will preferably be connected to the driving wheels via a gearbox and clutch system, or other form of drive train system, to achieve the transition from a stationary to a mobile state. The engine and drive train will best allow a range of actual vehicle road speed of between 1-350km/h, preferably between 5-130km/h and allow for continuous variation of speed thereof. The road speed of the vehicle is usually reduced by a braking mechanism fitted to the vehicle, the braking being generally applied by friction. The engine may either be air or water cooled, the air motion induced by a moving vehicle being used to directly, or indirectly cool the engine. The vehicle comprises a means to facilitate a change of vehicle direction, e.g. a steering wheel or stick. Usually at least 10% of the vehicle distance travelled is carried out at greater than 5km/h.

The engines using aviation gasoline are usually in piston driven aircraft, i.e. with at least one engine driving a means for mechanically moving air such as at least one propeller. Each engine usually drives at least one propeller driving shaft with 1 or 2

propellers. The aircraft may have 1-10 propellers e.g. 2-4. The aircraft engines usually have at least 2 cylinders, e.g. 2 to 28 cylinders, each of which is preferably greater than 700cc in volume, such as 700-2000cc e.g. 1310cc. The total engine size is usually 3700-50000cc e.g. 3700 to 12000cc for single or twin engined passenger light aircraft, 12000 to 45000cc for 2 or 4 engined freight or airline use (e.g. 15-200 passengers, such as 50 to 150 passengers). The engines may have an engine power to weight ratio of at least 0.3Hp/lb wt of engine, e.g. 0.3-2Hp/lb, and may have a power to cylinder volume of at least 0.5 (Hp/cu.in) e.g. 0.5-2. Cylinders may be arranged in rows, V formation, H formation, flat ('horizontally opposed') or radially around a common propeller drive shaft. One or more rows/circles of cylinders may be used, e.g. flat 2, flat 4, flat 6, V12, 12 or 3 circles of 7 cylinders etc. Every cylinder has one and more preferably at least two spark plugs. A gear system may optionally be used to drive the propeller and or a supercharger. Alternatively, an exhaust turbo charger may also be present. Exhaust outlets may be individual or run into a common manifold and preferably point in the opposite direction to forward flight. Fins may be present on the exterior of the engine for air cooling. Greater than 90% of the distance travelled by the engine, when in use, is usually spent at 500 feet or more above ground level. Typically, during greater than 90% of the time when the engine is running, the engine operates at above 1000rpm e.g. between 1000 to 3500 rpm.

The aircraft usually has at least one tank having a capacity of at least 100l, especially with a total capacity of at least 1000l. Small and micro-light aircraft may have tanks substantially smaller in capacity but can operate on the unleaded gasoline described.

The gasolines of the invention may be made in a refinery by blending the ingredients to produce at least 200,000l/day of gasoline such as 1-10million l/day. The gasoline may be distributed to a plurality of retail outlets for motor gasoline, optionally via wholesale or bulk outlets e.g. holding tanks, such as ones of at least 2 million l capacity e.g. 5-15 million l. The distribution may be by pipeline or in tanks transported by road, rail or water, the tanks being of at least 5000l capacity. At the retail sites e.g. filling station, the motor gasoline is dispensed to a plurality of users, i.e. the drivers of the vehicles, e.g. at a rate of at least 100 or 1000 different users per day. For aviation use, the gasoline is usually made in a refinery to produce at least 1000 barrels per day (or

100,000l/day) such as 0.1-2 million l/day. The avgas is usually distributed by tanker by road, rail or water, or pipelines directly to the airport distribution or holding tanks, e.g. of at least 300,000l capacity, from whence it is distributed by pipeline or tanker (e.g. a mobile refuelling bowser to fuel a plurality of aircraft, e.g. at least 5/day per tank; the aircraft may have one or more on-board tank each of at least 100l capacity.

The present invention is illustrated in the following Examples.

Examples 1-7

Various unleaded blends are made up with compound A1 and/or A2 and various refinery streams as shown in Table 1.

7 Formulated gasolines are made, each containing one of the above blends and a 15mg/l of a phenolic antioxidant 55% minimum 2,4 dimethyl-6-tertiary butyl phenol 15% minimum 4 methyl-2, 6-ditertiary-butyl phenol with the remainder as a mixture of monomethyl and dimethyl-tertiary butyl phenols.

In each case the gasolines are tested for MON and RON, and their Reid Vapour Pressure at 37.8°C. The results are shown in table 1, which also shows their analyses and distillation profile (according to ASTM D86).

Example 8

The emission characteristics on combustion of the formulated gasolines of Ex. 1-7 are determined.

The fuels are tested in a single cylinder research engine at a speed/load of 50/14.3rps/Nm with a LAMBDA setting of 1.01, and the ignition setting is optimised for the comparative blend. The emissions of CO, CO₂ total hydrocarbons, Nox, are measured from the exhaust gases. The results are averaged and show a reduction in the emissions compared to a standard unleaded fuel.

Example 9 and Comparative Ex. A

An unleaded blend was made up with 22446 pentamethyl heptane, blended with various refinery streams as shown in Table 3. Comp Ex. A, with heavy reformat meets the Europe 2005 requirement for high octane fuel with RON 97.0, MON 86.3 RVP at 37.8°C 54.7 kPa distillation profile according to ASTM D86, 10% evap, at 52.9°C 50% at 107.0°C and 90% at 166.1°C.

2 formulated gasolines were made, each containing one of the above blends and 15mg/l of the phenolic antioxidant used in Ex. 1-7.

In each case the gasolines were analysed. The results are shown in table 3.

The emission characteristics on combustion of the formulated gasolines of Ex. 9 and Comp. A were determined.

The fuels were tested as in Ex. 1-7 in a single cylinder research engine at a speed/load of 20/7/2rps/Nm with LAMBDA setting of 1.01, and the ignition setting was optimised for the comparative blend A. The emissions of CO, CO₂ total carbon oxides, total hydrocarbons, NO_x were measured from the exhaust gases as was the Fuel Consumption (expressed in g/h¹Whr). The results were averaged and compared to the comparative Ex.A. The degrees of change were as given in Table 4.

10

15

20

25

30

Table 3

	Comp A	8
	Base Fuel	
Formulation % v/v		
Butane	3	3
Full range catalytically cracked spirit	20	20
Alkylate	40	40
Light hydrocracked spirit	7	7
Full range steam cracked spirit	10	10
Heavy reformat	20	
2,2,4,4,6-Pentamethylheptane		20
Density kg/l	0.7487	0.7264
C:H	1 : 1.889	1 : 2.076
C% w/w	86.4	85.25
H% w/w	13.6	14.75
Benzene % v/v	0.6	0.6
Aromatics % v/v	29.4	9.4
Olefins % v/v	9.0	9.0

Table 4

Example	CO	CO ₂	CO _x	THC	NO _x	Fuel Economy
Comp A	0%	0.0%	0.0%	0.0%	0.0%	0.0%
9	-1.7%	-2.7%	-2.7%	3.1%	-4.5%	0.1%

5

Figures denote % change relative to base (Fuel (Comp.A))

Table 1

Ex.	1	2	3	4	5	6	7
Butane	47	36	54	28	2.9		
cpd A2	20.0	10.0	49.2	28.0	41.6	24.1	20.4
cpd A1	27.2	26.4	4.7	-	-		
Med Naphtha	7.4	0.07	27.3	48.0	17.9		23.7
Light Naphtha	43.2	60.6	13.6	1.5	-	41.1	35.4
Hydrocrackate						21.5	
Reformate						7.8	
Alkylate						5.6	
Steam Crack Spirit				19.7	37.6		20.4
% Aromatics	4.0	4.7	3.6	11.6	15.2		12.3
% Olefins	0.2	0.2	0.1	5.2	9.7		5.5
% Saturates	95.8	95.1	96.3	83.2	75.1		82.2
RON	110.0	104.5	110.0	95.0	110.0		95.0
MON	100.0	95.5	100.0	86.0	96.9		86.0
RVP.kPa	50.0	60.0	50.0	50.0	50.0		52.3
ROAD	105	100	105	90.5	103.45		90.5
E70% v/v	22.8	33.4	10.5	16.7	19.0		31.4
E100% v/v	49.9	60.0	49.0	49.0	51.1		53.5
E150% v/v	78.0	78.0	99.0	96.9	99.0		78.0
E180% v/v	92.8	92.6	100.0	99.8	100.0		93.2
Benzene % v/v	0.3	0.03	0.3	0.12	0.23		0.12
Sulphur % w/v				0.0005	0.0005		0.0004

Example 10

An unleaded blend was made up with 2,2,3,3-tetramethyl butane (12%), alkylate (45%), reformat (6%), isomerate (20%) and naphtha i.e. a straight sum gasoline (17%). The tetramethyl butane contained 86.6%, 2,2,3,3-tetramethyl butane, 3.6% 2,2,4-trimethyl pentane 3.7%, cis 3 methyl hexene 2 and 6% unknown and high boilers. It was made substantially according to the procedure of Marker and Oakwood J. Amer. Chem. Soc. 1938, 60, 258.

The blend was mixed with 15mg/l of the phenolic antioxidant used in Ex.1-3. The formulated gasoline was tested for MON and RON which were found to be 88.7 and 93.0 respectively, ROAD value 90.85.

15

20

25

30

Claims

1. Use of component (a), which is at least one branched chain alkane of 8-12 carbon atoms with at least 4 branches, which are methyl or ethyl, in an unleaded gasoline of MON at least 80 to reduce the emission levels on combustion of said gasoline.
2. A method of reducing emissions of exhaust gases in the combustion of an unleaded gasoline fuel of MON at least 80 which comprises having present in said gasoline at least 5 or 10% of component (a) as defined in claim 1.
3. Use in a spark ignition combustion engine of an unleaded gasoline fuel of MON at least 80 which comprises at least 5 or 10% of component (a) as defined in claim 1 to reduce emissions of exhaust gases.
4. Use or method according to any one of claims 1-3 wherein the gasoline is an unleaded motor gasoline.
5. Use or method according to any one of claims 1-3 wherein the gasoline is an unleaded aviation gasoline.
6. Use or method according to any one of the preceding claims wherein said gasoline comprises at least 10 or 15% in total by volume of said branched chain hydrocarbon.
7. Use or method according to claim 6 wherein said gasoline comprises at least 10 or 15% by volume of at least one branched chain hydrocarbon, which has 8-12 carbons and 4 methyl branches, and there being a minimum of at least 1,2, 5 or 10% by volume of at least one of such individual branched chain hydrocarbons.
8. Use or method according to claims 6 or 7 wherein the gasoline comprises 15-60% of said component (a).
9. Use or method according to any one of the preceding claims wherein in the said

branched chain hydrocarbon, there are 1, 2 or 3 pairs of geminal methyl branch substituents on a 4-6 carbon chain backbone, and if any ethyl CMe₂ structure is present, then there are 2 ethyl CMe₂ groups in the molecule, and no n-propyl group forms part of the backbone chain.

- 5 10. Use or method according to claim 9 wherein said branched chain hydrocarbon has 2 or 3 pairs of geminal methyl branches.
11. Use or method according to claim 10 wherein said hydrocarbon is at least one of 2,2,3,3-tetramethyl butane and 3,3,4,4-tetramethyl hexane.
12. Use or method according to any one of the preceding claims wherein said gasoline
10 comprises a blend composition with a MON value of at least 81 and RON value of at least 91 and also comprises at least one component (b), which is at least one liquid hydrocarbon or mixture thereof of bp60-160°C having a MON value of at least 70 and RON value of at least 90, the total amount of component (b) being at least 20%.
13. Use or method according to any one of claims 1-11 wherein said gasoline
15 comprises a composition of MON value at least 81 and RON value of at least 91 which also comprises at least one component (b) which is at least 20% in total of one or more refinery streams, such that said blend composition contains in total at least 70% of saturated hydrocarbons.
14. Use or method as claimed in any one of the preceding claims wherein the gasoline
20 or blend composition has RON value of 90-115, MON value of 85-105, aromatics content of less than 35%, olefins content of less than 14%, benzene less than 1%, % evaporated at 70°C 10-40%, % evaporated at 100°C 40-74%, % evaporated at 150°C 70-99.5 and RVP of 40-60 kPa
15. A formulated unleaded gasoline which comprises at least one motor or aviation
25 gasoline additive, and at least one of an unleaded gasoline of MON at least 80 and a blend composition, each as defined in any one of claims 1-14.
16. An unleaded gasoline according to claim 15 in which when the branched chain hydrocarbon is an alkane of 9 or 10 carbon atoms, then the blend composition contains less than 5% in total of 2,2,3-trimethyl pentane and 2,2,3-trimethyl butane.
- 30 17. A gasoline according to claim 15 or 16 which is a motor gasoline.
18. An unleaded blend composition having a Motor Octane Number (MON) of at least 81 and Research Octane Number (RON) of at least 91 which comprises component (a) a

total of at least 10% preferably at least 15% by volume of the blend composition of at least one branched chain hydrocarbon, which is an alkane of 8-12 carbon atoms with at least 4 methyl or ethyl branches (hereinafter called a compound (A)) there being a minimum of at least 1, 5 or 10% by volume (of the blend composition), of at least one individual compound (A), and component (b) at least one liquid hydrocarbon or mixture thereof of bp60-160°C having a MON value of at least 70 and RON value of at least 90, the total amount of component (b) being at least 20%.

19. A blend composition according to claim 18 wherein when the said branched chain hydrocarbon is an alkane of 9 or 10 carbon atoms, the blend contains at least 10% of an alkane of 6 or 7 carbons of MON at least 70 and RON at least 90.

20. An unleaded blend composition of MON value of at least 81 and RON value of at least 91 which comprises at least 10% component (a) as defined in claim 18 or 19 and as component (b) at least 20% in total of one or more refinery streams, such that the blend composition contains in total at least 70% of saturated hydrocarbons.

21. An unleaded blend composition according to any one of claims 18-20, wherein said hydrocarbon is as defined in any one of claims 9-11 or said composition is as defined in claim 14.

20

25

30

INTERNATIONAL SEARCH REPORT

Intern. al Application No

PCT/GB 00/03569

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 77130 A (PARKER ANTHONY GEORGE WILLIAM ;HOWARD PHILIP (GB); BP OIL INT (GB)) 21 December 2000 (2000-12-21) claims 1-6,9,11,12,18,20,21,23-25,27,28 ---	1-8, 12-21
A	WO 98 22556 A (BP OIL INT ;CLARK ALISDAIR QUENTIN (GB)) 28 May 1998 (1998-05-28) claims 1,6,14,15 table 1 ---	1-9, 12-15, 17,18, 20,21
P,X	EP 0 994 088 A (FORTUM OIL & GAS OY) 19 April 2000 (2000-04-19) claim 60 -----	1,3,4, 9-11,18, 19

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 January 2001

Date of mailing of the international search report

22/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

De Herdt, O

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/03569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0077130 A	21-12-2000	NONE	
WO 9822556 A	28-05-1998	AU 715896 B	10-02-2000
		AU 4878397 A	10-06-1998
		EP 0948584 A	13-10-1999
		GB 2334262 A	18-08-1999
		NO 992312 A	13-07-1999
		ZA 9710316 A	14-05-1999
EP 0994088 A	19-04-2000	FI 982250 A	17-04-2000
		AU 6344099 A	08-05-2000
		WO 0023402 A	27-04-2000